PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C11D 7/50

A1

(11) International Publication Number: WO 96/22356

(43) International Publication Date: 25 July 1996 (25.07.96)

(21) International Application Number: PCT/US96/00336

(22) International Filing Date: 11 January 1996 (11.01.96)

(30) Priority Data:

08/375,812	20 January 1995 (20.01.95)	US
08/573,416	15 December 1995 (15.12.95)	US

(81) Designated States: CA, CN, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(72) Inventors: FLYNN, Richard, M.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). GRENFELL, Mark, W.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). MOORE, George, G., I.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). OWENS, John, G.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(74) Agents: WEISS, Lucy, C. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(54) Title: CLEANING PROCESS AND COMPOSITION

(57) Abstract

A process for removing contaminants from the surface of a substrate comprises contacting the substrate with a cleaning composition comprising at least one mono-, di-, or trialkoxy-substituted perfluoroalkane, perfluorocycloalkane, perfluorocycloalkyl-containing perfluoroalkane, or perfluorocycloalkylene-containing perfluoroalkane compound, the compound optionally containing additional catenary heteroatoms. The compounds exhibit good solvency properties while being environmentally acceptable.

CLEANING PROCESS AND COMPOSITION

Field of the Invention

This invention relates to cleaning compositions comprising at least one partially-fluorinated ether compound and to processes for removing contaminants from substrate surfaces using such compositions. In another aspect, this invention relates to certain novel partially-fluorinated ether compounds. In yet another aspect, this invention relates to coating compositions comprising at least one partially-fluorinated ether compound and to processes for depositing coatings on substrate surfaces using such compositions.

Background of the Invention

Solvent cleaning applications where contaminated articles are immersed in (or washed with) solvent liquids and/or vapors are well-known. Applications involving one or more stages of immersion, rinsing, and/or drying are common. Solvents can be used at ambient temperature (often, accompanied by ultrasonic agitation) or at elevated temperatures up to the boiling point of the solvent.

A major concern in solvent cleaning is the tendency (especially where solvent is used at an elevated temperature) for solvent vapor loss from the cleaning system into the atmosphere. Although care is generally exercised to minimize such losses (e.g.,

WO [illegible]

European Patent Publication No. 0 450 855 A2 (Imperial Chemical Industries PLC) describes the use of low molecular weight, fluorine-containing ethers of boiling point 20-120°C in solvent cleaning applications.

International Patent Publication No. WO 93/11280 (Allied-Signal, Inc.) discloses a non-aqueous cleaning process which utilizes a fluorocarbon-based rinsing solvent.

U.S. Patent No. 5,275,669 (Van Der Puy et al.) describes hydrofluorocarbon solvents useful for dissolving contaminants or removing contaminants from the surface of a substrate. The solvents have 4 to 7 carbon atoms and have a portion which is fluorocarbon, the remaining portion being hydrocarbon.

U.S. Patent No. 3,453,333 (Litt et al.) discloses fluorinated ethers containing at least one halogen substituent other than fluorine and states that those ethers which are liquid can be used as solvents for high molecular weight resinous perhalogenated compounds such as solid polychlorotrifluoroethylene resins.

French Patent Publication No. 2,287,432 (Societe Nationale des Poudres et Explosifs) describes new partially-fluorinated ethers and a process for their preparation. The compounds are said to be useful as hypnotic and anesthetic agents; as monomers for preparing heat-stable, fire-resistant, or self-lubricant polymers; and in phyto-sanitary and phyto-pharmaceutical fields.

German Patent Publication No. 1,294,949 (Farbwerke Hoechst AG) describes a technique for the production of perfluoroalkyl-alkyl ethers, said to be useful as narcotics and as intermediates for the preparation of narcotics and polymers.

Summary of the Invention

In one aspect, this invention provides a process for removing contaminants (e.g., hydrocarbons, fluorocarbons, or even water) from the surface of a substrate (e.g., metal, glass, ceramic, plastic, or fabric). The process comprises contacting the substrate with (or exposing the substrate to) a liquid- and/or vapor-phase cleaning composition comprising at least one mono-, di-, or trialkoxy-substituted perfluoroalkane, perfluorocycloalkane, perfluorocycloalkyl-containing perfluoroalkane, or perfluorocycloalkylene-containing perfluoroalkane compound. The compound can optionally contain additional catenary (i.e., in-chain) heteroatoms (e.g., oxygen or nitrogen) and preferably has a boiling point in the range of from about 25°C to about 200°C.

have
surface

The alkoxy-substituted compounds used in the process of the invention exhibit unexpectedly high stabilities in the presence of acids, bases, and oxidizing agents. In addition, in spite of their fluorine content, the compounds are surprisingly good solvents for hydrocarbons (as well as fluorocarbons). The compounds are low in toxicity and flammability, have ozone depletion potentials of zero, and have short atmospheric lifetimes and low global warming potentials relative to chlorofluorocarbons and many chlorofluorocarbon substitutes. Since the compounds exhibit good solvency properties while being environmentally acceptable, they satisfy the need in the art for substitutes or replacements for the commonly-used cleaning solvents which have been linked to the destruction of the earth's ozone layer.

In other aspects, this invention also provides certain novel mono-, di-, and trialkoxy-substituted perfluorocompounds; a cleaning composition;

substituted ammonium (mono-, di-, tri-, or tetra-substituted), or quaternary phosphonium salts, and mixtures thereof. Such salts are in general commercially available but, if desired, can be prepared by known methods, e.g., those described by M. C. Sneed and R. C. Brasted in Comprehensive Inorganic Chemistry, Volume Six (The Alkali Metals), pages 61-64, D. Van Nostrand Company, Inc., New York (1957), and by H. Kobler et al. in Justus Liebigs Ann. Chem. 1978, 1937. 1,4-diazabicyclo[2.2.2]octane and the like are also suitable solid nucleophiles.

The cleaning process of the invention can be carried out by contacting a contaminated substrate with a cleaning composition comprising at least one of the above-described alkoxy-substituted perfluorocompounds. The perfluorocompounds can be utilized alone or in admixture with each other or with other commonly-used cleaning solvents, e.g., alcohols, ethers, alkanes, alkenes, perfluorocarbons, perfluorinated tertiary amines, perfluoroethers, cycloalkanes, esters, ketones, aromatics, siloxanes, hydrochlorocarbons, hydrochlorofluorocarbons, and hydrofluorocarbons. Such co-solvents can be chosen to modify or enhance the solvency properties of a cleaning composition for a particular use and can be utilized in ratios (of co-solvent to perfluorocompound(s)) such that the resulting composition has no flash point. Preferably, the perfluorocompound(s) used in the composition have boiling points in the range of from about 25°C to about 200°C, more preferably from about 25°C to about 125°C.

The cleaning composition can be used in either the gaseous or the liquid state (or both), and any of the known techniques for "contacting" a substrate can be utilized. For example, a liquid cleaning composition can be sprayed or brushed onto the

substrate, a gaseous cleaning composition can be blown across the substrate, or the substrate can be immersed in either a gaseous or a liquid composition. Elevated temperatures, ultrasonic energy, and/or agitation can be used to facilitate the cleaning. Various different solvent cleaning techniques are described by B. N. Ellis in <u>Cleaning and Contamination of Electronics Components and Assemblies</u>, Electrochemical Publications Limited, Ayr, Scotland, pages 182-94 (1986).

Very good reference

Both organic and inorganic substrates can be cleaned by the process of the invention. Representative examples of the substrates include metals; ceramics; glass; polycarbonate; polystyrene; acrylonitrile-butadiene-styrene copolymer; natural fibers (and fabrics derived therefrom) such as cotton, silk, fur, suede, leather, linen, and wool; synthetic fibers (and fabrics) such as polyester, rayon, acrylics, nylon, and blends thereof; fabrics comprising a blend of natural and synthetic fibers; and composites of the foregoing materials. The process is especially useful in the precision cleaning of electronic components (e.g., circuit boards), optical or magnetic media, and medical devices.

The cleaning process of the invention can be used to dissolve or remove most contaminants from the surface of a substrate. For example, materials such as light hydrocarbon contaminants; higher molecular weight hydrocarbon contaminants such as mineral oils and greases; fluorocarbon contaminants such as perfluoropolyethers, bromotrifluoroethylene oligomers (gyroscope fluids), and chlorotrifluoroethylene oligomers (hydraulic fluids, lubricants); silicone oils and greases; solder fluxes; particulates; and other contaminants encountered in precision, electronic, metal, and medical device cleaning can be removed.

The process is particularly useful for the removal of hydrocarbon contaminants (especially, light hydrocarbon oils), fluorocarbon contaminants, particulates, and water (as described in the next paragraph).

To displace or remove water from substrate surfaces, the cleaning process of the invention can be carried out as described in U.S. Patent No. 5,125,978 (Flynn et al.) by contacting the surface of an article with a liquid cleaning composition which preferably contains a non-ionic fluoroaliphatic surface active agent. The wet article is immersed in the liquid composition and agitated therein, the displaced water is separated from the liquid composition, and the resulting water-free article is removed from the liquid composition. Further description of the process and the articles which can be treated are found in said U.S. Patent No. 5,125,978. The process can also be carried out as described in U.S. Patent No. 3,903,012 (Brandreth).

This invention also provides a cleaning composition comprising (a) a major amount (preferably, at least about 60 percent of the composition by weight) of at least one mono-, di-, or trialkoxy-substituted perfluoroalkane, perfluorocycloalkane, perfluorocycloalkyl-containing perfluoroalkane, or perfluorocycloalkylene-containing perfluoroalkane compound, the compound optionally containing additional catenary heteroatoms; and (b) a minor amount of at least one co-solvent selected from the group consisting of alcohols, ethers, alkanes, alkenes, perfluorocarbons, perfluorinated tertiary amines, perfluoroethers, cycloalkanes, esters, ketones, aromatics, siloxanes, hydrochlorocarbons, hydrochlorofluorocarbons, and hydrofluorocarbons. Preferably, the co-solvent is selected from the group

consisting of alcohols, alkanes, alkenes, cycloalkanes, esters, aromatics, hydrochlorocarbons, and hydrofluorocarbons.

Representative examples of co-solvents which can be used in the cleaning composition include methanol, ethanol, isopropanol, t-butyl alcohol, methyl t-butyl ether, methyl t-amyl ether, 1,2-dimethoxyethane, cyclohexane, 2,2,4-trimethylpentane, n-decane, terpenes (e.g., a-pinene, camphene, and limonene), trans-1,2-dichloroethylene, methylcyclopentane, decalin, methyl decanoate, t-butyl acetate, ethyl acetate, diethyl phthalate, 2-butanone, methyl isobutyl ketone, naphthalene, toluene, p-chlorobenzotrifluoride, trifluorotoluene, hexamethyl disiloxane, octamethyl trisiloxane, perfluorohexane, perfluoroheptane, perfluorooctane, perfluorotributylamine, perfluoro-N-methyl morpholine, perfluoro-2-butyl oxacyclopentane, methylene chloride, chlorocyclohexane, 1-chlorobutane, 1,1-dichloro-1-fluoroethane, 1,1,1-trifluoro-2,2-dichloroethane, 1,1,1,2,2-pentafluoro-3,3-dichloropropane, 1,1,2,2,3-pentafluoro-1,3-dichloropropane, 2,3-dihydroperfluoropentane, 1,1,1,2,2,4-hexafluorobutane, 1-trifluoromethyl-1,2,2-trifluorocyclobutane, 3-methyl-1,1,2,2-tetrafluorocyclobutane, and 1-hydropentadecafluoroheptane.

The above-described alkoxy-substituted perfluorocompounds can be useful not only in cleaning but also in coating deposition, where the perfluorocompound functions as a carrier for a coating material to enable deposition of the material on the surface of a substrate. The invention thus also provides a coating composition and a process for depositing a coating on a substrate surface using the composition. The process comprises the step of

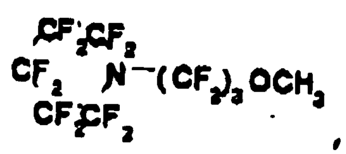
applying to at least a portion of at least one surface of a substrate a coating of a liquid coating composition comprising (a) a solvent composition comprising at least one mono-, di-, or trialkoxy-substituted perfluoroalkane, perfluorocycloalkane, perfluorocycloalkyl-containing perfluoroalkane, or perfluorocycloalkylene-containing perfluoroalkane compound, the compound optionally containing additional catenary heteroatoms; and (b) at least one coating material which is soluble or dispersible in the solvent composition. The solvent composition can further comprise one or more co-dispersants or co-solvents (as defined supra, preferably those having boiling points below about 125°C) and/or one or more additives (e.g., surfactants, coloring agents, stabilizers, anti-oxidants, flame retardants, and the like). Preferably, the process further comprises the step of removing the solvent composition from the coating by, e.g., allowing evaporation (which can be aided by the application of, e.g., heat or vacuum).

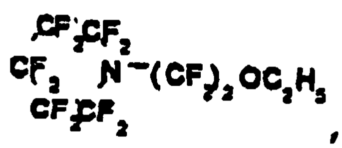
Coating materials which can be deposited by the process include pigments, lubricants, stabilizers, adhesives, anti-oxidants, dyes, polymers, pharmaceuticals, release agents, inorganic oxides, and the like, and combinations thereof. Preferred materials include perfluoropolyether, hydrocarbon, and silicone lubricants; amorphous copolymers of tetrafluoroethylene; polytetrafluoroethylene; and combinations thereof. Representative examples of materials suitable for use in the process include titanium dioxide, iron oxides, magnesium oxide, perfluoropolyethers, polysiloxanes, stearic acid, acrylic adhesives, polytetrafluoroethylene, amorphous copolymers of tetrafluoroethylene, and combinations thereof. Any of the substrates described above (for

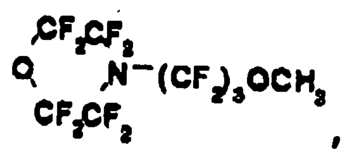
e claim:

1. A process for removing contaminants from the surface of a substrate comprising the step of contacting a substrate with a liquid- and/or vapor-phase cleaning composition comprising at least one mono-, di-, or trialkoxy-substituted perfluoroalkane, perfluorocycloalkane, perfluorocycloalkyl-containing perfluoroalkane, or perfluorocycloalkylene-containing perfluoroalkane compound, said compound optionally containing one or more additional catenary heteroatoms.

2. A process for removing contaminants from the surface of a substrate comprising the step of contacting a substrate with a liquid- and/or vapor-phase cleaning composition comprising at least one compound selected from the group consisting of $c\text{-}C_6F_{11}CF_2OC_2H_5$, $c\text{-}C_6F_{11}CF_2OCH_3$, $4\text{-}CF_3\text{-}c\text{-}C_6F_{10}CF_2OCH_3$,


,


,


, $CH_3OCF_2\text{-}c\text{-}C_6F_{10}CF_2OCH_3$, $C_4F_9OC_2H_5$, $C_4F_9OCH_3$, $c\text{-}C_6F_{11}OCH_3$, $(CF_3)_2CFCF_2OCH_3$, $(CF_3)_2CFCF_2OC_2H_5$, $C_8F_{17}OCH_3$, $C_2F_5CF(OCH_3)CF(CF_3)_2$, $CF_3CF(OCH_3)CF(CF_3)_2$, $C_5F_{11}OCH_3$, $C_5F_{11}OC_2H_5$, and $C_3F_7OCH_3$.

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 450 855 A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 91302893.5

(22) Date of filing: 27.03.91

(51) Int. Cl.^{5}: C11D 7/50

(30) Priority: 04.04.90 GB 9007645

(43) Date of publication of application:
09.10.91 Bulletin 91/41

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB IT LI NL SE

(71) Applicant: IMPERIAL CHEMICAL INDUSTRIES PLC
Imperial Chemical House, Millbank
London SW1P 3JF (GB)

(72) Inventor: Winterton, Neil
Copper Pine, Carmel Hill
Pantasaph, Holywell, Clwyd CH8 8NZ (GB)
Inventor: McBeth, David George
51 Marina Village
Preston Brook, Runcorn, Cheshire WA7 3BH (GB)

(74) Representative: Thomas, Ieuan et al
Imperial Chemical Industries PLC, Legal Department: Patents, PO Box 6, Bessemer Road
Welwyn Garden City, Herts, AL7 1HD (GB)

(54) Solvent cleaning of articles.

(57) Low molecular weight, fluorine-containing ethers of boiling point 20°C to 120°C are used in solvent cleaning applications.

	Boiling Point (°C)
1,1-difluoroethyl methyl ether	47
1,1,2,2-tetrafluoroethyl methyl ether	36.5
1-chloro-1,2,2-trifluoroethyl methyl ether	70.6
1-1-dichloro-2,2-difluoroethyl methyl ether	104.8
1-chloro-2,2-difluoroethyl methyl ether	27.5 [1]
1,1,1,2,3,3-hexafluoropropyl methyl ether	54.5
1,1-difluoroethyl ethyl ether	65
1,1,2,2-tetrafluoroethyl ethyl ether	56
1-chloro-1,2,2-trifluoroethyl ethyl ether	82 [2]
1,1,1,2,3,3-hexafluoropropyl ethyl ether	64.5
1,1,2,2-tetrafluoroethyl n-propyl ether	71.7 [3]
1-chloro-1,2,2-trifluoroethyl n-propyl ether	109
1,1,1,2,3,3-hexafluoropropyl n-propyl ether	92
1-chloro-1,2,2-trifluoroethyl isopropyl ether	100
1-chloro-2,2-difluoroethyl isopropyl ether	53 [4]
1,1,1,2,3,3-hexafluoropropyl isopropyl ether	76
1,1,2,2-tetrafluoroethyl n-butyl ether	49 [5]
1,1,1,2,3,3-hexafluoropropyl n-butyl ether	108
1,2,2-trifluoroethyl 1,1,1-trifluoroethyl ether	75
1,1,2,2-tetrafluoroethyl 1,1-difluoroethyl ether	77
di(1,1-difluoroethyl) ether	103
1-chloro-1,2,2-trifluoroethyl 1,1-difluoroethyl ether	102
1,1,2,2-tetrafluoroethyl 1,1-di(trifluoromethyl)methyl ether	85

[1] At 130 mm Hg
[2] At 630 mm Hg
[3] At 637 mm Hg
[4] At 121 mm Hg
[5] At 113 mm Hg

Mixtures of ethers, including azeotropic mixtures, may be used if desired as may mixtures of an ether with one or more cosolvents. The same cosolvents may be used as are used with the principal solvents in known cleaning applications and in particular polar compounds such as alcohols are preferred cosolvents. Cleaning compositions comprising the ether and a cosolvent, notably a lower alkanol cosolvent, are provided according to another feature of the invention. Azeotropic mixtures of ethers and alcohols represent preferred embodiments of the invention. Lower aliphatic alcohols containing 1 to 4 carbon atoms are useful in such mixtures.

generally will not require stabilisation against degradation. However, stabilisers may be added if desired or if required for particularly onerous cleaning applications and the stabilisers used in the common solvents may be employed, notably nitroalkanes and epoxides.

The ethers may be used as replacements for the solvent(s) used in any of the known cleaning applications and have the advantage of being generally more stable towards aluminium than the solvents they replace. The ethers may be used to replace part of the solvent(s) used in known cleaning applications.

The invention is illustrated by the following examples.

EXAMPLE 1

This Example illustrates the use of 2-chloro-1,1,2-trifluoroethyl methyl ether in cleaning flux residues from copper-coated boards.

A known weight of solder cream was applied to test boards (5 cm x 7 cm) cut from copper-coated FR4 (epoxy/glass fibre laminate) board and the cream was reflowed in a MICRO VPS soldering unit. The solder cream used was a 62% tin/38% lead solder available as Multicore PRAB 3.

2-chloro-1,1,2-trifluoroethyl methyl ether (boiling point 65°C at 630mm Hg) was boiled in a beaker fitted with an upper cooling coil through which cold water was circulated to create a boiling liquid phase and a vapour phase and the contaminated board was dipped into the boiling liquid for 60 seconds and then held in the vapour for 30 seconds.

Residual ionic contamination of the test board, expressed as mg sodium chloride per square centimetre was determined using a Protonique Contaminometer. The ionic contamination of an unwashed test board was determined and the % removal of ionic contamination was calculated. 61% of the ionic flux residues were removed from the test boards.

The ether was heated to 190°C and the vapour pressures above the ether were determined over the range 50 - 190°C. A slight increase in vapour pressure was observed at approximately 120°C but there was no visible evidence of solvent breakdown at this temperature.

In a Comparative Test, using 1,1,2-trichloro-1,2,2-trifluoroethane as the solvent. 45% of the ionic flux residues were removed.

EXAMPLE 2-3

These Examples illustrate the use of mixtures of 2-chloro-1,1,2-trifluoroethyl methyl ether and methanol for cleaning flux residues from copper coated printed circuit boards.

In Example 2, a mixture of 2-chloro-1,1,2-trifluoroethyl methyl ether and methanol was boiled until a constant boiling mixture was obtained. This azeotrope contained 18.5% by weight of methanol and boiled at 56.8°C at normal pressure.

The azeotropic mixture was used to remove ionic residues from the test boards as described in Example 1. 66.9% of the ionic resudes were removed.

In Example 3, the procedure of Example 2 was repeated except that a mixture of the ether (95% by weight) and methanol (5% by weight) was used instead of the azeotropic mixture. 68.1% of the ionic residues were removed.

EXAMPLE 4

This Example demonstrates the stability of 2-chloro-1,1,2- trifluoroethyl methyl ether in the presence of aluminium.

The ether was refluxed in contact with aluminium for 48 hours. The aluminium test piece was partly immersed in the liquid and partly in the vapour above the liquid.

In the test, no increase in chloride ion or fluoride ion was observed in the liquid phase and the GC trace of the solvent after the test showed no change. There was no significant weight change in the metal test piece which emerged from the test clean and bright with no evidence of corrosion.

The results demonstrate that the ether has high stability in the presence of aluminium and is suitable for use in aluminium cleaning applications. Stabilisers may be added to inhibit the build up of acidity in the ether when it is used to clean metals.

EXAMPLE 5

ated boards.

Tetrafluoroethyl methyl ether, boiling point 33-35°C (630 mm Hg) and density (25°C) 1.28g/ml, was used to clean flux residues from copper coated boards as described in Example 1. 82% of the ionic flux residues were removed.

EXAMPLE 6-8

These Examples illustrate certain azeotropic mixtures suitable for use in the process according to the present invention.

Tetrafluoroethyl methyl ether forms an azeotrope with methanol containing 4% by weight methanol and boiling at 34.5°C.

The ether forms an azeotrope with 1,1,2-trichloro-1,2,2 -trifluoroethane containing 38.5% by weight of the haloethane and boiling at about 34.9°C.

The ether forms a ternary azeotrope with 1,1,2-trichloro- 1,2,2-trifluoroethane and methanol containing 41% by weight of the haloethane and 3% by weight of methanol and boiling at about 34.6°C.

EXAMPLE 9

This Example illustrates the use of a ternary azeotropic mixture in the process according to the present invention.

The ternary azeotropic mixture of tetrafluoroethyl methyl ether, 1,1,2-trichloro-1,2,2-trifluoroethane and methanol prepared in Example 8 was used to remove solder flux residues from circuit boards by the procedure described in Example 1. 48.2% of the ionic flux residues were removed.

EXAMPLE 10-11

These Examples illustrate further azeotropic mixtures for use in the process according to the present invention.

Tetrafluoroethyl ethyl ether, boiling point 56°C and density 1.21 g/ml, forms an azeotrope with methanol containing 10.8% by weight of methanol and boiling at 48.6°C.

The ether forms an azeotrope with ethanol containing 38.5% by weight of 1,1,2-trichloro-1,2,2-trifluoroethane and boiling at 46.3°C.

Claims

1. A process for cleaning articles which comprises contacting the articles with a solvent composition comprising a low molecular weight fluorine-containing ether of boiling point in the range of about 20°C to about 120°C, or the vapour thereof or both

2. A process for cleaning article/s as claimed in Claim 1 wherein the ether contains at least 3 carbon atoms.

3. A process for cleaning articles as claimed in Claim 1 carried out at elevated temperature.

4. A process for cleaning articles as claimed in Claim 1 wherein the said ether has a boiling point in the range of from 25°C to 80°C.

5. A process as claimed in Claim 1 wherein the solvent composition further comprises a co-solvent.

6. A process as claimed in Claim 5 wherein the co-solvent is a lower alkanol having up to 4 carbon atoms.

7. A process as claimed in Claim 6 wherein the ether and the alcohol form an azeotropic mixture.

8. A solvent composition as defined in any one of Claims 5-7.

9. A solvent cleaning composition is claimed in Claim 8 wherein the low molecular weight fluorine containing ether of boiling point in the range of about 20°C to about 120°C is at least
2-chloro-1,1,1,2-trifluoroethyl methyl ether, tetrafluoroethyl methyl ether, or tetrafluoroethyl ethyl ether

10. A solvent cleaning composition as claimed in Claim 9 in the form of an azeotrope wherein the co-solvent is at least one of methanol, ethanol or 1,1,2-trichloro-1,2,2-trifluoroethane.

This invention relates to solvent cleaning applications in which contaminated articles such as, for example, metals, textiles, glass, plastics, electronic components and printed circuit boards are cleaned using a solvent or solvent vapour and more particularly to the use of low molecular weight ethers as solvents in solvent cleaning applications.

Solvent cleaning applications wherein contaminated articles are immersed in or washed with halogenated hydrocarbon solvents and/or the vapours thereof are well known and are in common use. Applications involving several stages of immersion, rinsing and drying are common and it is well known to use the solvent at ambient temperature (often accompanied by ultrasonic agitation) or at an elevated temperature up to the boiling point of the solvent. Examples of solvents used in these cleaning processes are 1,1,2-trichloro-1,2,2-trifluoroethane, 1,1,1-trichloroethane, trichloroethylene, perchloroethylene and methylene chloride. These solvents are used alone or in mixtures with cosolvents such as aliphatic alcohols or other low molecular weight, polar additives and depending to some extent upon the articles to be cleaned are often stabilised against degradation induced by light, heat and the presence of metals.

In the known common solvent cleaning applications and especially in those applications where the solvent is used at an elevated temperature, there is a tendency for solvent vapour to be lost from the cleaning system into the atmosphere. Further losses may occur in loading and unloading the solvents into cleaning plant and in recovering used solvent by distillation. Whilst care is usually exercised to minimize losses of solvent into the atmosphere, for instance by improved plant design and vapour recovery systems, the expense of totally preventing losses is exhorbitant and most practical cleaning applications result in some loss of solvent vapour into the atmosphere.

Until recently, the use of the common cleaning solvents has been regarded as safe practice in that the solvents are stable, of low toxicity, non-flammable materials believed to be environmentally benign. However recent evidence suggests that some at least of the common solvents may have a long-term deleterious effect on the stratosphere, the so-called ozone layer, so that a replacement solvent is seen to be desirable.

According to the invention there is provided the use in solvent cleaning applications of solvents comprising low molecular weight fluorine-containing ethers of boiling point in the range of about 20°C to about 120°C.

The ether has a boiling point in the range 20°C to 120°C, preferably from 25°C to 85°C, such that it may be used in conventional and existing cleaning equipment. For any particular cleaning application, an ether may be selected having a boiling point close to that of the solvent the ether is replacing.

The ethers can be obtained by reaction of a halogenated aliphatic olefin with an optionally halogenated aliphatic alcohol in known manner and thus contain at least three carbon atoms in the molecule. Usually the ether will contain not more than five carbon atoms although it may contain six or more carbon atoms providing its boiling point is below about 120°C.

The ether contains at least one and will usually contain two or more fluorine atoms but will not generally be perfluorinated. In addition to fluorine atoms, the ether may contain chlorine atoms, bromine atoms and hydrogen atoms. Ethers containing chlorine and/or hydrogen may contain one or two chlorine atoms and/or one or two hydrogen atoms.

Examples of alcohols which may be used to produce the ethers are methanol, ethanol, propanol and butanol and halogenated derivatives thereof. Alkenes which may be used include tetrafluoroethylene, hexafluoropropene, chlorotrifluoroethylene and the chlorofluoropropenes and hydrogen-containing analogues of these compounds for example trifluoroethylene and chlorodifluoroethylene.

Examples of ethers which may be used, and their boiling points, include the following:-